



Hydrogen-free catalytic depolymerization of waste polyolefins at mild temperatures

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ABSTRACT

Reductive methods of polyolefin waste deconstruction such as hydrogenolysis/hydrocracking have enabled advances in plastic upcycling at low temperatures. However, these processes require hydrogen gas, presenting economic and environmental tradeoffs. Here, we present an overview of recent developments in low-temperature, hydrogen-free depolymerization of polyolefins. We start by introducing technologies that utilize sacrificial solvents to cleave C-C bonds, followed by progress in solvent-free depolymerization. We then provide an overview of catalytic processes in petroleum and lignin upgrading that may be extended to polyolefin activation and depolymerization, including alkane dehydrogenation/aromatization, transfer hydrogenation, and hydrogen co-generation, as well as opportunities for utilizing the polymer itself as a hydrogen source. Next, we provide an overview of techniques for quantifying reaction progress via hydrogen consumption and for characterizing the degree of unsaturation of polyolefins. We close with an outlook on the role of feedstock treatment, economic analysis, and process optimization in ushering in these new technologies.

1. Introduction

The complexity of plastic waste streams and inconsistent infrastructure for efficient recycling has resulted in a multitude of research challenges which are being approached with the goal of keeping plastics in a circular economy. These challenges include advanced mechanical recycling and compatibilization, functionalization and repurposing, and chemical deconstruction to higher value chemicals and/or monomers. Chemical deconstruction can be driven by bio-, photo-, electrochemical, and thermal catalysis. Thermal catalytic processes involving the forming and breaking of carbon-carbon bonds are relevant to the petroleum industry and have long been studied in the heterogeneous catalysis community. Consequently, the increasing global interest in plastic waste remediation has drawn the attention of the community towards the application of hydrocarbon chemistries for polyolefin deconstruction. There are many desirable process targets associated with activating and breaking C-C bonds in polyolefin waste, including high selectivity towards value-added products, operation at low temperatures and pressures, minimal and benign solvent use, ease of separations, use of stable and inexpensive catalysts, favorable economics, and a low environmental footprint.

Reductive methods of cleaving C-C bonds including hydrogenolysis

and hydrocracking have emerged as promising low-temperature depolymerization processes, producing high yields of liquid hydrocarbons (~40–90%) and operating between 200 and 300°C [1–9]. Hydrogenolysis and hydrocracking typically require expensive catalysts containing Pt and Ru [4,7,10–12], although recent studies have employed less expensive alternatives like Zr- and Ni-based catalysts [13–15]. Despite promising avenues for lowering the catalyst cost, the need to supply molecular hydrogen is a potential detriment to the overall economic and environmental viability of these processes.

Currently, most molecular hydrogen is produced using fossil fuel feedstocks. Approximately 62% of hydrogen produced in 2021 was sourced from natural gas, while 18% was produced from naphtha and 19% from coal [16]. Less than 1% of hydrogen produced in 2021 was classified as low-emissions, most of which was still sourced from fossil fuels but implemented carbon capture, utilization and storage (CCUS) post processing [16]. These added carbon emissions reduce the positive impact of depolymerization technologies dependent on hydrogen, and would limit their viability as estimated via broad-scope life cycle assessments [17]. Additional challenges are presented by the storage and transportation of hydrogen, especially if the hydrogen is not generated on-site. Large-scale storage of hydrogen is difficult, as hydrogen has relatively low volume density and high flammability [18]. At a pressure

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of 100 bar, hydrogen only has a density of 7.8 kg/m^3 at ambient temperatures, and storing reasonable amounts of it requires a large amount of space [19]. While high-pressure hydrogen vessels can withstand operating pressures up to 800 bar, they are very expensive to produce [18–21]. These issues make hydrogen particularly problematic in industrial applications and it is likely that the emerging plastics upcycling industry will face these same challenges.

The increasing demand for molecular hydrogen is another consideration in evaluating the situations in which plastics depolymerization technologies may be applicable. As seen in Fig. 1, hydrogen is already in high demand in the oil refining, ammonia, methanol, and iron and steel industries, being consumed at rates of $38 \text{ MtH}_2/\text{yr}$, $31 \text{ MtH}_2/\text{yr}$, $12 \text{ MtH}_2/\text{yr}$, and $4 \text{ MtH}_2/\text{yr}$, respectively [20]. Not only are these industries projected to grow and therefore increase the demand for hydrogen, but new technological developments have led some industries to employ additional hydrogen-demanding processes. These include the personal transportation, shipping, aerospace and aviation, and heating industries, among others [20,22,23]. With hydrogen in such demand, it is an important factor when evaluating appropriate technologies for regional implementation. In areas where hydrogen is more readily accessible, perhaps hydrogenolysis is a more appropriate plastics upcycling technology. In regions with a less steady supply of hydrogen, hydrogen-free depolymerization technologies may be more viable.

From these consistent issues with hydrogen production distribution and demand, it is worth considering chemical recycling solutions which avoid hydrogen altogether. This includes solutions which not only avoid the consumption of hydrogen in their primary reactions, but also minimize use for tangential purposes such as treating the active catalyst or driving dehydrogenation steps. Pyrolysis is a technology which does not require a supply of molecular hydrogen, enabling the deconstruction of plastic in an inert environment to produce relatively high liquid hydrocarbon yields (around 20–80% depending on the plastic). But this process requires high temperatures (up to 800°C) and potentially elevated pressures [24,25]. There are several recent reviews which have already highlighted developments in pyrolysis [24–28]. Some additional reviews have also explored the topic of C–O bond breakage, as seen in the depolymerization of polyethylene terephthalate (PET), including glycolysis, methanolysis, and hydrolysis [29–31]. Given the existing coverage and perspectives on these technologies, we shift our focus instead to recent progress in utilizing tandem chemistries to activate C–C bonds at relatively low temperatures in the absence of molecular hydrogen. Thus, this perspective will present an overview of recent developments in low-temperature hydrogen-free depolymerization of

polyolefins with the aim of identifying key opportunities for improving selectivity while decreasing the environmental footprints of these processes (Fig. 2). The topics covered will include co-fed solvent depolymerization in absence of molecular hydrogen, hydrogen- and solvent-free depolymerization, existing industrial processes as potential inspiration for plastics upcycling, and the characterization of polymer unsaturation and hydrogen transfer.

2. Hydrogen-free depolymerization using co-fed solvents

The activation of polyolefins such as polyethylene (PE) is difficult due to their strong backbones and lack of functional handles for depolymerization. The insertion of olefinic groups into PE backbones can provide a means of C–C bond activation, which can be cleaved via metathesis or ethenolysis with a sacrificial substrate. In this section, we will highlight a few recent developments for the depolymerization of PE in the absence of molecular hydrogen with the addition of alkanes or ethylene, and some important considerations for advancement and implementation of these technologies.

Cross metathesis of alkanes with PE has emerged as a method of breaking the polymer into a distribution of hydrocarbons in the liquid and wax range. Olefin metathesis over both homogeneous and heterogeneous catalysts has seen a wide variety of applications including drug discovery and development, disproportionation reactions in petroleum upgrading, and polymerization reactions [36–38]. Metathesis of alkanes is also achievable by a sequence of dehydrogenation to olefins, followed by olefin metathesis, and finally re-hydrogenation back to alkanes [39]. While the initial dehydrogenation step is unfavorable thermodynamically, the combination of metathesis catalysts with active hydrogenation/dehydrogenation catalysts drives the reaction forward. In 2016, Jia et al. demonstrated the application of tandem catalytic cross alkane metathesis towards the depolymerization of PE with n-alkanes (n-hexane, n-octane) or petroleum ether under mild conditions ($150\text{--}175^\circ\text{C}$, 2–96 h) to produce varying distributions of light alkanes ($\text{C}_3\text{--C}_7$), diesel ($\text{C}_9\text{--C}_{22}$), and higher alkanes/waxes [40]. The authors combined a supported “pincer”-ligated iridium complex with $\text{Re}_2\text{O}_7/\gamma\text{-Al}_2\text{O}_3$ to drive dehydrogenation/hydrogenation and metathesis reactions, respectively. An overview of the process of depolymerizing PE with alkanes is shown in Fig. 3a, where the alkane and PE undergo dehydrogenation, followed by metathesis, then re-hydrogenation. As the cycle continues and the short alkanes are consumed, the molecular weight distribution shifts towards intermediate chain lengths in the diesel range. The authors demonstrated the successful depolymerization of a variety of PE substrates, including high-density polyethylene (HDPE), low-density polyethylene (LDPE), linear low-density polyethylene (LLDPE), a used PE bottle, and a used PE film.

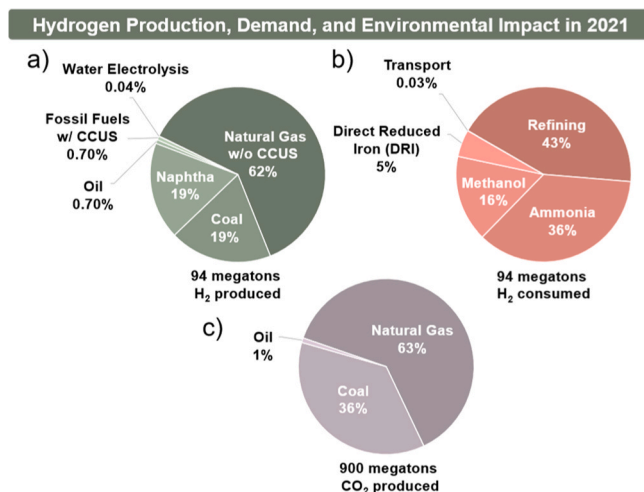


Fig. 1. Summary of the hydrogen market in 2021: a) Sources of hydrogen production; b) Demand for hydrogen by industry; c) Carbon dioxide produced by major industrial methods.

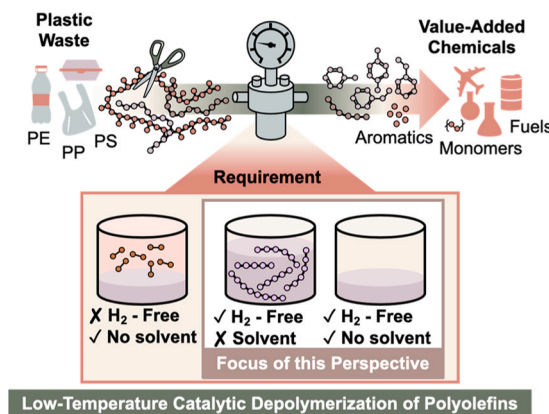


Fig. 2. Focus of this perspective – an overview and outlook on plastics upcycling with a focus on hydrogen-free cleavage of C–C bonds at mild temperatures in the presence and absence of solvents or co-feeds.

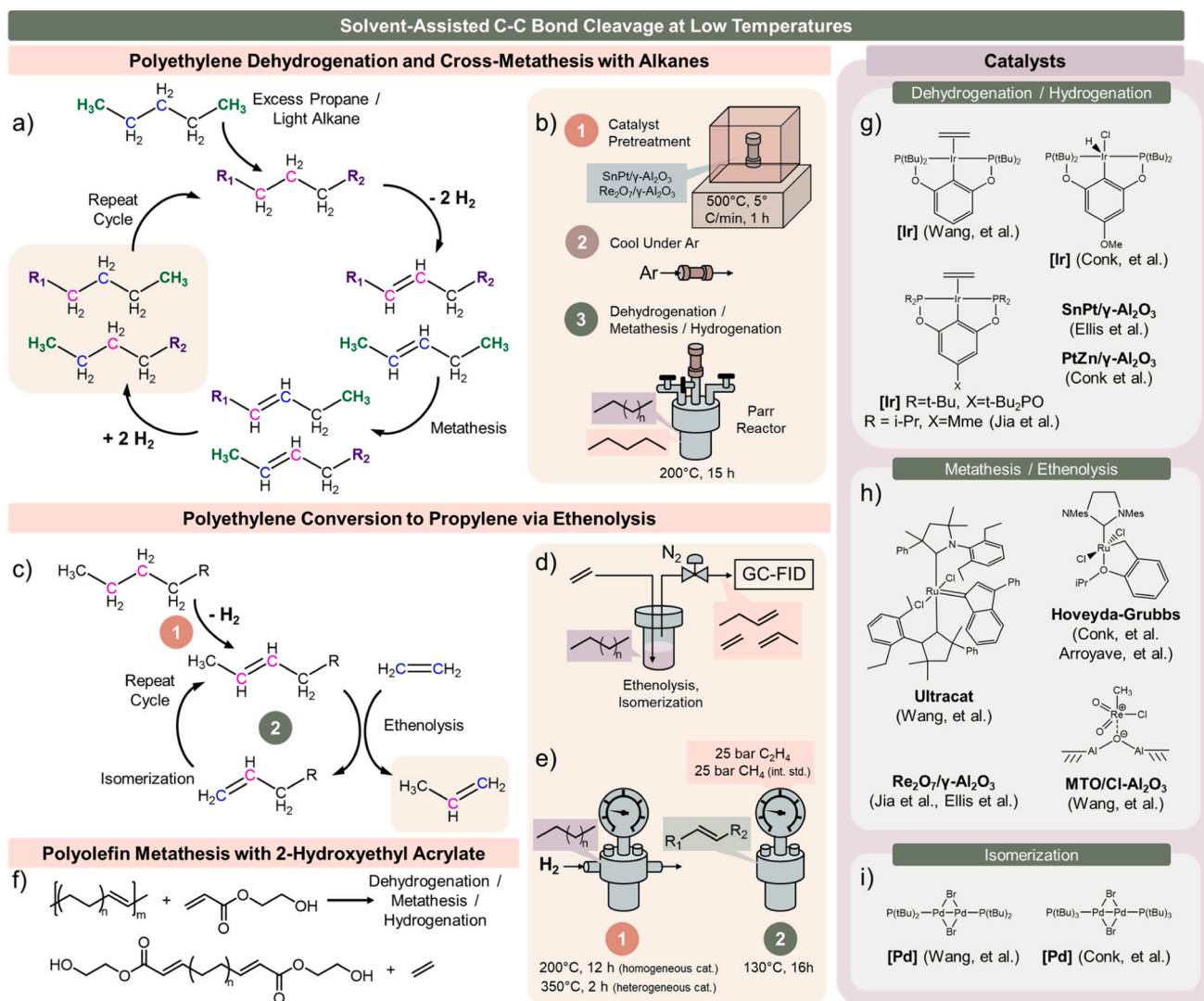


Fig. 3. Overview of recent technologies for the depolymerization of polyolefins using sacrificial solvents and co-fed hydrocarbons in the absence of hydrogen gas: a) Overview of the tandem dehydrogenation and olefin cross metathesis strategy for depolymerization of polyethylene; b) Catalyst treatment and reactor set-up for the process in a); c) Overview of the ethenolysis process for the depolymerization of polyethylene; d) Reactor set-up for ethenolysis / isomerization by Wang et al. [33]; e) Reactor set-up for dehydrogenation / ethenolysis by Conk et al. [34]; f) Overview of the dehydrogenation/ cross metathesis/ hydrogenation strategy employed by Arroyave et al. [35]; g) Homogeneous and heterogeneous dehydrogenation / hydrogenation catalysts; h) Homogeneous and heterogeneous metathesis / ethenolysis catalysts; i) Homogeneous isomerization catalysts.
(a) Adapted from Ellis et al. [32].

Recently, Ellis et al. demonstrated that the depolymerization of PE with n-pentane via tandem dehydrogenation and olefin cross metathesis could be achieved with a fully heterogeneous catalytic system [32]. Instead of using Ir pincer catalysts for hydrogenation/dehydrogenation, the authors employed a SnPt/γ-Al₂O₃ catalyst and demonstrated that a physical mixture of SnPt/γ-Al₂O₃ and Re₂O₇/γ-Al₂O₃ was effective in depolymerizing a linear PE substrate at 200 °C, resulting in a molecular weight decrease of 73% over 15 h. The general procedure for this study is shown in Fig. 3b, where the catalysts are first pretreated in a muffle furnace under atmosphere at 500 °C for 1 h (12 °C/min ramp rate). After pretreatment, and due to their air sensitivity, the treated catalysts are immediately transferred into a purge system with ultra-high purity (UHP) argon and allowed to cool to room temperature. The catalyst is then added along with PE and n-pentane to a Parr reactor, which is then purged with argon and brought to temperature. The final depolymerized product was characterized by high temperature gel permeation chromatography (HT-GPC) and gas chromatography (GC) for the high and low molecular weight hydrocarbons, respectively. The authors noted

that the post-reaction catalyst was coated in carbonaceous deposits and posited that this could lead to long-term decreases in activity. Since then, Kim et al. demonstrated that tungsten oxide supported on silica (WO_x/SiO₂) is an effective metathesis catalyst for the molecular redistribution of LDPE with n-decane in tandem with Pt/γ-Al₂O₃ for dehydrogenation/ hydrogenation. This catalyst was able to achieve complete conversion of the polyolefin after 3 h at 300 °C, with some noticeable coke formation [41]. The resulting products, in the C₃ to C₃₅ range, can be used in a broad range of applications from gasoline to lubricating oils. Hernandez et al. performed a technoeconomic analysis (TEA) study concerning the feasibility of various chemical recycling techniques including hydrogenolysis, which produces lubricant-range products like those produced through the tandem dehydrogenation/metathesis route. The authors estimated a minimum selling price (MSP) of \$1.67/kg product, which falls within the range of between \$1.5 and \$1.8/kg for the current fossil-based route. [42] A more comprehensive TEA of the metathesis-based route towards producing lubricants is necessary to compare the economic feasibility to the hydrogenolysis and fossil-based

processes, especially given the high feedstock cost.

Ethenolysis has also recently emerged as a method of cleaving the carbon-carbon bonds in polyolefins. In 2020, Guirionnet and Peters published a conceptual paper exploring the kinetics of a tandem reaction which combined olefin metathesis and double bond isomerization steps to convert PE into propylene [43]. The authors developed a model by transforming thousands of coupled rate equations, pseudo-steady-state approximations, and local density approximations into a solvable equation with the Fokker-Planck form, from which predictions of propylene formation rates and evolution of molecular weight distributions as a function of time may be predicted. In 2022, Wang et al. experimentally demonstrated that PE can be converted into propylene using ethylene through tandem olefin metathesis and isomerization [33]. The general strategy for ethenolysis is shown in Fig. 3c, and the experimental set-up from Wang et al. is shown in Fig. 3d. The authors used a series of both homogeneous and heterogeneous ethenolysis, isomerization, and dehydrogenation/isomerization catalysts for rapid olefin metathesis in combination with rate-limiting isomerization in a semi-continuous flow reactor with excess ethylene operating between 70 and 100 °C. The chosen substrate was monounsaturated PE of relatively low molecular weight ($M_n = 3000$ Da), as the reaction required PE chains with at least one C=C bond. The authors were able to achieve high selectivity to propylene ($\geq 94\%$) and showed that either homogeneous (Ir-based) or heterogeneous (Pt/ γ - Al_2O_3) catalysts could be employed for the transfer hydrogenation of PE to convert ethylene to ethane. This route is promising because it demonstrates the potential to monomerize PE into propylene, which can be repolymerized back into polypropylene (PP) to enable a circular economy. Finally, the authors noted that, when employing the heterogeneous ethenolysis catalyst (MTO/Cl- Al_2O_3), deactivation occurred after only 7–15 h. This indicates that further research is necessary to improve catalyst lifetime. A preliminary life cycle analysis (LCA) indicated a potential saving of 13 MT/y in CO₂-equiv GHG emissions [33]. Still, the process economics remain uncertain. In a preliminary economic analysis, Guirionnet and Peters estimated that propylene products are worth ~\$0.2–0.3/mol more than the ethylene reactants; however, this was under the assumption that the PE is free [43]. In reality, even though plastic is generally seen as waste and therefore zero-cost, processible PE which has been cleaned and purged of additives and contaminants is expensive and therefore a major factor in determining process economics [44].

Conk et al. also investigated the cleavage of PE with co-fed ethylene, and demonstrated that PE can be deconstructed into propylene via partial dehydrogenation followed by tandem isomerizing ethenolysis of the unsaturated chain [34]. Fig. 3e shows the experimental setup, where in the first step, PE is dehydrogenated using either homogeneous Ir-pincer complexes or heterogeneous Pt-Zn/Silica catalysts. In the second step, metathesis and isomerization are catalyzed by second-generation Hoveyda-Grubbs catalysts and $[PdP(tBu)_3(m-Br)]_2$, respectively. This study offers a promising means of deconstructing PE into monomers with yields over 80%. The homogeneous dehydrogenation step could be carried out at 200 °C, however the heterogeneous analogue required a temperature of 350 °C. It should be noted that while H₂ is not consumed, it is used in the initial dehydrogenation step, obscuring its classification as a hydrogen-free process. In addition to efforts to improve compatibility with contaminated waste streams [45], additional investigation into active heterogeneous systems may improve the scalability of this process. Ir-pincer catalysts are effective for dehydrogenation chemistries [46] and progress has been made in the heterogenization of these materials to produce recyclable catalysts. For example, Huang et al. developed highly active and recyclable heterogeneous Iridium pincer catalysts for the transfer dehydrogenation of alkanes [47]. The implementation of these highly active and recoverable catalysts may enable the scalability of this process while maintaining activity at low temperatures.

Zeng et al. developed a strategy to convert PE into divinyl-functionalized oligomers via a multi-step process in which PE is

brominated with Br₂, followed by dehydrobromination under an inert atmosphere to produce vinylene PE, followed by ethenolysis [48]. While this process operates at mild temperatures (~100 °C) and does not require high pressures of H₂ gas, the process requires toxic Br₂. Preliminary technoeconomic analysis by the authors also revealed that the profitability of the process is highly sensitive to Br₂ and solvent recovery, which may present challenges in scalability.

The utilization of olefins as a functional handle for depolymerization creates opportunities in metathesis reactions with a variety of plastic substrates, solvents, and/or co-feeds. Arroyave et al. recently reported a method of converting HDPE into telechelic macromonomers via HDPE dehydrogenation followed by cross-metathesis with 2-hydroxyethyl acrylate and subsequent re-hydrogenation [35]. The depolymerization process is shown in Fig. 3f. After producing the macromonomers, the product was repolymerized through transesterification to generate a polymer which had comparable mechanical properties to the initial HDPE. This strategy combines depolymerization with functionalization for circular reprocessing, as the re-manufactured polymer has functional handles installed for tunable mechanical properties and depolymerization.

In Fig. 3g-i we summarize structures of the dehydrogenation / hydrogenation, metathesis / ethenolysis, and isomerization catalysts used. The tradeoffs between activity and recoverability are a major factor when considering the energy requirements for these processes as well as the scalability. Even when recoverable, catalysts composed of Ru, Pt, Ir, Re, and Pd are expensive and have low earth abundance. Furthermore, the air sensitivity of these catalysts introduces complications in process scalability and catalyst regeneration. The application of atomically-dispersed heterogeneous catalysts with well-defined active sites offers a promising means of catalyzing low-temperature depolymerization of polyolefins as well as the metathesis of alkanes and olefins, while minimizing precious metal loading and maintaining recoverability [49].

In addition to the catalyst, the feedstock is a large cost driver in process economics [44]. Expanding the substrate scope beyond PE and monounsaturated PE could enable the conversion of polyolefins like polypropylene (PP) and polystyrene – or even synthetic rubbers like polybutadiene – into propylene. While rubbers are not easily melt-processible, the unsaturation provides a functional handle for metathesis reactions. The ability to process mixed plastic substrates would also be desirable to lower the cost of feedstock separations. The framework of “catalytic funneling,” where a mix of plastic materials are reprocessed into a single value product, is an attractive application of the propylene synthesis reaction [50]. In addition to expanding the scope of plastic substrates, the process economics could be further improved by utilizing renewable (eg. bio-derived), sustainable, or waste feedstocks as sacrificial solvents or hydrogen sources. For example, hydrogenolysis of waste PE or PP generates a distribution of linear and/or branched alkanes with varying carbon chain lengths depending on the extent of reaction [1,3,4]. Using the shorter-chain alkane fraction as a sacrificial solvent for the cross metathesis of polyolefins could enable more control over the molecular weight distributions and thus valorize both the solvent and polyolefin. To expand the metathesis depolymerization route to substrates with branches such as PP, catalysts must be selected based on how effectively they can activate substituted and branched C-C bonds. Chabanas et al. developed a Re-based heterogeneous catalyst for olefin metathesis that is highly active even for functionalized olefins, enabling metathesis of both terminal and internal olefins and substrates spanning from methyl oleate to isobutene [51]. These metathesis-based solvent-assisted methods hold promise for integration into a circular economy, particularly for their potential to monomerize waste plastic into propylene.

3. Hydrogen-free and solvent-free depolymerization

While promising, depolymerization with co-feeds, cross-metathesis, and other solvent-dependent methods can be potentially limited in

scalability by the cost and waste associated with solvent use. It is thus beneficial to also examine approaches which avoid the consumption of both molecular hydrogen and co-fed solvents. Among these approaches is the direct aromatization of polymers to alkyl aromatics, as these aromatics have found uses as lubricants, engine oils, refrigeration fluids, and insulating oils, and more [52]. The production of aromatics from waste polyolefins has the potential to create other high-value products such as solvents, benzene / toluene / xylenes (BTX), and could even meet targets for sustainable aviation fuel [53].

In an exciting development for hydrogen-free and solvent-free depolymerization, Zhang et al. demonstrated that a Pt/ γ -Al₂O₃ catalyst could convert PE into long-chain alkyl-aromatics (avg. C₃₀) at 280 °C over 24 h in an inert argon environment [54]. The authors attributed this to a tandem hydrogenolysis/aromatization pathway. The overall reaction and proposed mechanism are shown in Fig. 4a, where the PE chain can undergo a variety of dehydroaromatization, ring opening/closure, hydrogenation/dehydrogenation, and transfer hydrogenolysis steps, producing cyclic products and aromatic products with varying alkyl chain lengths, which were characterized using GPC (with RI and UV detectors), field desorption mass spectrometry (FD-MS), and ¹H and ¹³C NMR. Despite the moderate reaction temperature, the overall reaction is thermodynamically accessible due to the combination of endothermic aromatization with exothermic hydrogenolysis. As with the reaction set-ups for dehydrogenation and cross metathesis, these experiments were also performed with procedures to minimize exposure to air (Fig. 4b). The ability of the Pt/ γ -Al₂O₃ to catalyze the transfer of hydrogen from the substrate itself to drive hydrogenolysis is an encouraging development for hydrogen-free depolymerization chemistries. Furthermore, the authors show that the catalyst can be reused for multiple cycles, although there is some loss in activity due to decreasing active platinum surface area. The catalyst stability, long reaction times (24 h), and use of a precious metal catalyst leave room for improvement in the economic feasibility of this reaction.

In a recent study Zichittella et al. discovered that cobalt oxide nanoparticles (5 wt% Co) supported on Brønsted-acidic zeolite ZSM-5 (Co/ZSM-5) were able to catalyze the selective conversion of PE, PP, and mixtures of PE/PP into propane via hydrocracking at 250 °C and

70 bar H₂, over a 20 h period [55]. While the focus of the paper was on hydrocracking, some activity was also reported in a control reaction with a purely nitrogen environment. Interestingly, under these conditions, Co/ZSM-5 catalyzed the conversion of PE into gaseous products including propane, as well as mixtures of aromatics including benzene, toluene, ethylbenzene, xylenes, and alkyl aromatics (Fig. 4c). Despite the low product selectivity and the fact that the catalyst suffered some coking in the absence of H₂, this reaction demonstrated the feasibility of producing aromatic hydrocarbons from PE at low temperatures without supplying H₂ and with a more earth-abundant metal. Lee et al. investigated polyolefin and model PE (*n*-hexadecane) depolymerization over silica-alumina-based catalysts and found that Brønsted-acidic zeolites ZSM-5 and Y were able to catalyze the depolymerization of *n*-hexadecane under 45 bar N₂, at 375 °C over 2 h to produce C₃-C₁₆ hydrocarbons [56]. Despite the lack of molecular hydrogen, the hydrogen atoms in the polymer itself can be transferred, affording both saturated and unsaturated products. Reactions performed in the absence of hydrogen [55], or with the absence of metal (Co, or Ni) to active hydrogen, produce products with a distinct yellow color which is indicative of the formation of unsaturated products.

While these processes do not consume hydrogen during reaction, many of the catalyst pretreatment steps require reduction in H₂, which is worth considering when labeling a process as “hydrogen-free.” Investigation into various combinations of metals and supports, including Brønsted and Lewis acidic supports, as well as mild catalyst synthesis and pretreatment processes, could lead to further developments in transfer hydrogenation and hydrogenolysis under mild conditions.

4. Inspiration from petroleum and lignin upgrading

Past and ongoing research on petroleum refining and lignin utilization can serve as inspiration for novel technologies in the realm of plastics upcycling. Petroleum and biomass research focusing on olefin aromatization, transfer hydrogenation, and cogeneration of hydrogen, among others, offers details which could be key in developing technologies for depolymerizing PE, PP, and other plastics.

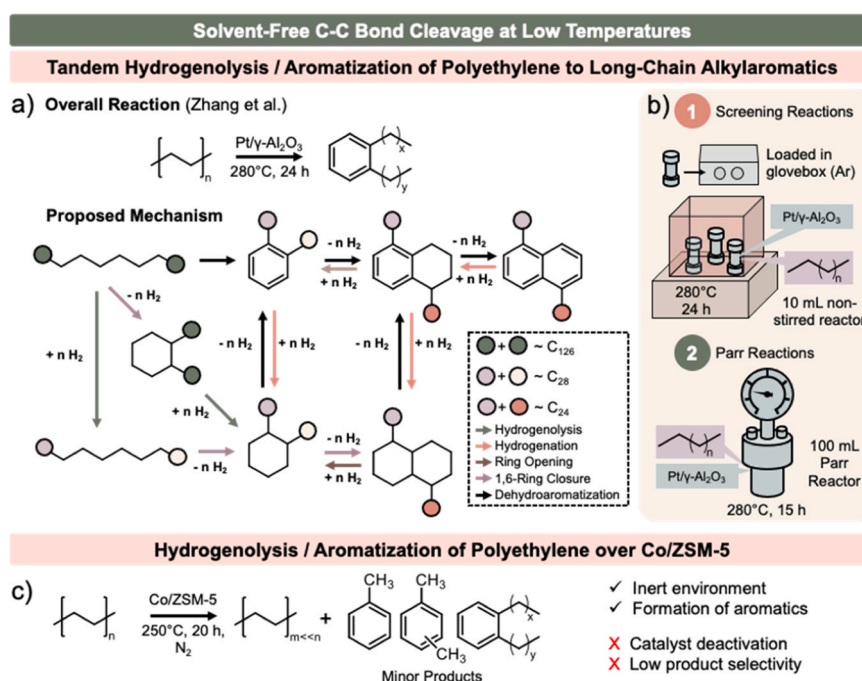


Fig. 4. Progress in solvent-free cleavage of C-C bonds at low temperatures: a) Tandem hydrogenolysis/ aromatization of polyethylene to long-chain alkylaromatics; b) Catalyst treatment and reactor set-up for the process in a); c) Hydrogenolysis/aromatization of polyethylene over Co/ZSM-5 [55].

(a) Adapted from Zhang et al. [54].

4.1. Dehydrogenation/aromatization

The aromatization of short-chain alkanes is a major theme in petroleum upgrading research. Literature on this subject may offer crucial kinetic and mechanistic clues about aromatizing longer-chain polyolefins. Therefore, procedures from these studies, including reaction conditions and catalyst usage, can be used to inform and inspire research in the plastics domain. Table 1 lists a selection of specific studies and their conditions, with mechanisms for the aromatization of hexane and octane shown in Figs. 5a and 5b. These reactions, operating between 300°C and 600°C, employ numerous catalysts typically composed of a metal – such as Ga, Ag, Zn, Mo, or Pt – supported on metal oxides or zeolites. We point the reader towards additional reviews which demonstrate the wide applicability of aromatization [57–59]. It is worth considering, however, that polyolefins have much different chemical and mass transfer properties than short-chain alkanes and olefins, which can affect the range of operating conditions and the mechanisms of chain cleavage [60]. Additionally, as the chain lengths of molecules increase, the distribution of unique hydrocarbon products will continue to grow. Strategies such as chemical lumping analysis may be employed to provide an understanding of the evolution of feedstock and product compositions [61–63]. Some of these aromatization processes require additional reagents such as hydrogen and methane or inert gases such as helium. These co-feeds may serve multiple purposes – for instance, He et al. noted that the use of methane, especially at higher pressures around 70 atm, drove the product selectivity towards larger aromatic compounds when compared to control reactions with nitrogen [64]. This was explained as being a result of the participation of methane in the co-aromatization process, which becomes more feasible on the external surface of the catalyst at higher pressures. As for n-octane aromatization, hydrogen may serve several purposes, such as maintaining catalytic activity and generating metal hydrides which may improve hydrogenation; however, too much hydrogen may also result in the reversal of the dehydrogenation pathway or the promotion of hydrocracking [65,66]. The use of gaseous co-feeds may be a limiting factor in these methods' applicability to depolymerization due to the cost associated with purchasing and storing these reagents.

4.2. Transfer hydrogenation/hydrogenolysis in biomass and lignin systems

Discoveries in transfer hydrogenation observed in lignin splitting and other biomass fractionation show potential in translation to polyolefin depolymerization. In the absence of gaseous hydrogen, C-O bond-splitting reactions require hydrogen from other sources. In native biomass fractionation, it has been shown that hydrogen used in hydrogenation can be sourced from co-fed alcohols [73–75] and formic acid [76]. Other solvents, such as glycerol, can also be used as hydrogen donors for lignin splitting [77]. Notably, lignin splitting by use of both homogeneous catalysts including pincer, acidic, and basic catalysts [78,

79], as well as some effective heterogeneous analogs of these catalysts, has been achieved [80,81]. Some groups have found that lignin splitting is possible by a mechanism of lignin self-donating hydrogen [82,83], which is a noteworthy observation that has profound implications for plastics upcycling. With the proof of concept in biomass splitting, it may then be possible to control reaction conditions to enable self-hydrogen donation in polyolefin depolymerization. For example, Fig. 5c illustrates the activation of poly(1-hexene) (PH) and PE via transfer hydrogenation of norbornene demonstrated by Ray et al. at 150 °C using an Ir-based catalyst [84]. For PH, the authors were able to achieve selective dehydrogenation of the backbone, with up to 18% unsaturation per repeat unit. For PE, they achieved up to 4.4% unsaturation per repeat unit. After unsaturation, the next hypothetical step towards C-C bond cleavage could employ either metathesis or ethenolysis. Vardon et al. demonstrated that both saturated and unsaturated fatty acids could be catalytically converted into hydrocarbons via hydrogenation and decarboxylation, removing saturation via the addition of hydrogen and acid functional groups via C-C bond cleavage [85]. Interestingly, they were also able to generate hydrogen in-situ via glycerol reforming, commenting that improvements in the aqueous phase reforming of glycerol may cause a net zero or even net positive production of molecular hydrogen. Additional potential hydrogen donating sources are shown in Fig. 5d. By investigating and applying some of these biomass upgrading strategies with co-fed solvents to plastics upcycling, it may be possible to further reduce the environmental footprint of depolymerization processes. However, an important consideration when borrowing transfer hydrogenation discoveries from biomass literature is the added problem of creating multiphase systems. Considering that polyolefin melts are often immiscible in many of these polar sacrificial solvents, it will be important to improve miscibility to accomplish transfer hydrogenation. Furthermore, the miscibility of polymer melts in polar sacrificial solvents can be significantly altered in the presence of additives like compatibilizers, [86] and by addition of different polymers, forming polymer blends which possess different physical properties [87]. These factors highlight the importance of improving miscibility to accomplish transfer hydrogenation in a well-mixed manner.

4.3. Cogeneration of H₂

Besides direct transfer hydrogenation, processes which require hydrogen could potentially utilize molecular hydrogen produced by cogeneration processes. Supercritical water gasification (SCWG), for instance, can be used to produce hydrogen from biomass and organic matter [88,89] and could potentially be used in tandem with a hydrogen-dependent depolymerization plant to process both organic and plastic wastes. Additionally it has been shown that wax (n-paraffin) can be used in direct catalytic hydrogen production at slightly lower temperatures and pressures than SCWG [90,91]. Molecular hydrogen could also be cogenerated by waste plastics pyrolysis [92], effectively

Table 1
Summary of various alkane/alkene aromatization processes and their conditions, conversions, and yields.

Reagent	Catalyst	Reaction Time	Temperature	Pressure	Conversion	Yield	Reference
ethylene	ZSM-5 with Ga, Ag, Zn	1–20 hr	300–650°C	1 atm He	10–85%	10–50% BTX	Uslamin et al.[67]
propylene	Ag-Ga/ZSM-5	1 hr	400°C	12–70 atm CH ₄ , N ₂	1.8–3.8%	0–30% benzene, toluene, C ₈ to C ₁₂	He et al.[64]
n-octane	Pt on K-BEA, K-MAZ, K-FAU	1–16 hr	500°C	1 atm H ₂	8.0–37.7%	15.4–65.3% BTX, ethylbenzene	Jongpatiwuta et al. [68]
n-octane	Pt-Zn/UZSM-5	1 hr	400°C	20 atm CH ₄	46.2–99.4%	23.1–65.7% BTX, C ₉ to C ₁₂	He et al.[69]
n-octane	Pt/KL zeolites	2 hr	500°C	1 atm H ₂	8.9–28.3%	50–80% BTX, ethylbenzene	Trakarnroek et al.[70]
n-octane	Mo ₂ C on Al ₂ O ₃ , SiO ₂ , ZSM-80, ZSM-280	10 hr	500–600°C	1 atm Ar	11.5–100.0%	5–85% BTX	Széchenyi et al.[71]
n-hexane	Ga/ZSM-5	1–12 hr	550°C	1 atm H ₂ , N ₂	-	30–60% BTX	Thivasasith et al.[72]

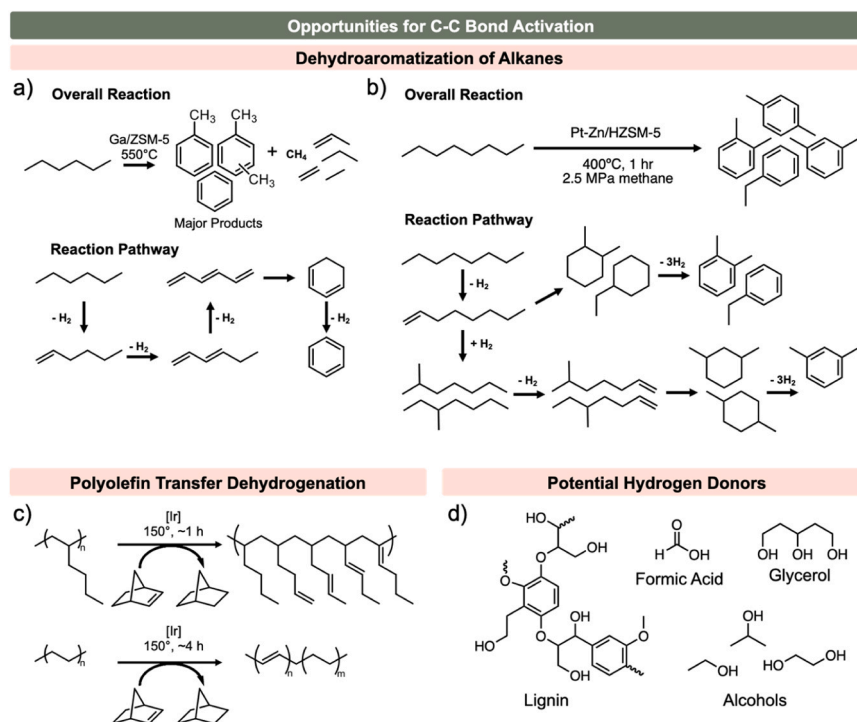


Fig. 5. Opportunities and inspiration for activating and cleaving C-C bonds: a) Overall reaction and pathway for dehydroaromatization of hexane, b) Overall reaction and pathway for dehydroaromatization of octane; c) Transfer hydrogenation of norbornene from poly(1-hexene) and PE; d) Potential hydrogen donors for solvent-assisted depolymerization.

(a) adapted from Thivasasith et al. [72]. (b) adapted from He et al. [69]. (c) adapted from Ray et al. [98].

splitting a plastic wastes processing plant into two sections: one for pyrolysis and one for low-temperature hydrogenolysis. Plasma-assisted hydrogen production from PE has also been demonstrated, however the high energy cost is a limiting factor in applicability [93]. Finally, strides have been made in hydrogen storage and production from the decomposition of liquid organic hydrogen carriers (LOHCs) such as formic acid [94]. Formic acid is safer and easier to store than hydrogen gas and can be decomposed on-site to meet hydrogen needs [95]. It can be made sustainably from hydrogen and carbon dioxide [95] as well as various forms of biomass [96]. However, these methods of hydrogen storage are limited in scope by the economics of formic acid-forming catalysts, thermodynamic preference for the undesirable dehydration reaction, and CO₂ capture technology [95,97].

5. Quantification and probing of hydrogen consumption and transfer

In hydrogenolysis or hydrocracking reactions of polyolefins, where all of the products are saturated hydrocarbons, direct tracking of the amount of hydrogen in the reactor headspace can be used as a metric for the amount of carbon-carbon bonds cleaved [11,55]. In that case, each molecule of H₂ consumed cleaves one C-C bond, so the conversion of hydrogen can be directly linked to the total number of catalytic turnovers. This is an important metric when comparing activity across different catalysts and reaction conditions, as selectivity towards different hydrocarbon chain lengths is affected by cascade reactions from multiple C-C bond cleavage events. If the turnovers are not normalized, this can lead to misleading conclusions about the intrinsic selectivity of a given process. Hydrogen consumption in the headspace can be measured using gas chromatography equipped with a thermal conductivity detector (TCD) or mass spectrometer (MS) in tandem with either an internal standard in the headspace and/or careful tracking of the initial and final pressure of the gas produced in batch reactions.

When aromatic or unsaturated products are formed from polyolefins,

the assumption that one H₂ consumed equals one bond cleaved no longer holds, because hydrogen from the polymer itself could be produced and consumed to drive hydrogenolysis, or hydrogen could be produced as a result of dehydrogenation or aromatization. Thus, to track turnovers it becomes necessary to characterize not only the change in molecular weight of the starting polymer but also the aromatic content and extent of unsaturation in the chain.

The predominating methods of characterizing the extent of unsaturation are hydrogen and carbon nuclear magnetic resonance (¹H NMR and ¹³C NMR) [99]. Both have been applied to evaluate the saturation of polymers and other compounds like lipids [100–102]. These methods enable identification and relative quantification of each hydrogen and carbon functional groups – such as vinyl, end, etc. – which can provide a clear understanding of the saturation characteristics of a given polyolefin. Likewise, ¹H NMR has also been used to estimate the extent of hydrogenation of branched alkene polymers [98].

Fourier-transform infrared spectroscopy (FTIR) is also useful for characterizing saturation in polyolefins [103,104]. This includes the evaluation of vinyl groups conjugated with main-chain double bonds [105]. While FTIR can reveal the presence or absence of carbon-carbon double bonds, it can be difficult to use the method alone to quantify the extent of unsaturation due to the effects of both conjugation and placement of the double bonds [106,107]. The extent of saturation has also been evaluated using elemental analysis (EA), also known as CHNX, which is a characterization method that measures the relative amounts of carbon, hydrogen, nitrogen, and heteroatoms in a given sample. By keeping track of this compositional information, the empirical formula, and therefore the degree of unsaturation, can be calculated [108–110].

Thermogravimetric analysis has been used to distinguish different varieties of LDPE among other polymers, indicating properties like molecular weight and density [111]. It may also be able to indicate the degree of unsaturation of a given polymer by comparing differences in thermal stability [112]. Another potential method of measuring unsaturation in a polymer is to measure hydrogen uptake via hydrogenation

(but not deconstruction) of the polymer to measure the hydrogen required to re-saturate the bonds. The evaluation of the crystalline structure of a given polyolefin using techniques like SAXS and WAXS is also well-founded [113,114]. Variations in the degree of saturation of these materials, as well as their degree of branching and their method of crystallization, may impact the resulting scattering profiles. This can be seen when comparing the SAXS/WAXS results of polymers like polyethylene, natural rubber, and polyisoprene [115,116]. These direct and indirect methods of characterizing and quantifying the polyolefin and degrees of unsaturation are summarized in Fig. 6. In addition to unsaturation, we encourage the consideration of the extent of backbone scission versus demethylation as well as conversion to ensure that the bond-splitting effectiveness of different catalysts can be correctly compared [117]. This offers a more normalized view of catalytic activity and reveals each catalyst's intrinsic selectivity.

6. Conclusions and outlook

In this review, we have identified promising catalytic techniques for the deconstruction and upcycling of polyolefin waste at low temperatures and without the consumption of molecular hydrogen, highlighting processes that require solvents or co-feeds and those that do not. These processes build on catalytic hydrocarbon processing techniques like metathesis, hydrogenation/dehydrogenation, and aromatization. Insights from petroleum and lignin upgrading can be used to accelerate advancements in the selective hydrogen-free depolymerization of polyolefins at mild conditions. Depending on the pathway selected, these reactions may enable the production of hydrocarbons in the lubricant, gasoline, and diesel ranges as well as monomers like propylene. Among the considerations when extending these technologies to plastics is the characterization of the polymer itself, both to track the extent of depolymerization and the degrees of unsaturation.

As discussed throughout this review, effective catalyst design requires consideration of cost of materials, cost of synthesis, stability, reusability, and appropriate matching of active sites to the material's existing functional handles. Many highly effective and stable catalysts such as Pt/ γ -Al₂O₃ are comprised of expensive noble metals, which present challenges when scaling up due to their rarity and high cost. The development of novel catalysts composed of more earth-abundant materials, which mimic the effects of noble metal sites while maintaining activity and stability, is an ongoing area of research. It is also important to minimize the cost of and hydrogen use during the synthesis,

pretreatment, and regeneration of the catalysts. Another crucial part of designing catalysts will be synthesizing materials with active sites tailored to the polymer feedstocks. In the hydrogenolysis of polyethylene, the only functional handles available are C-C bonds; to cleave these, one must first activate molecular hydrogen via a metal or metal-like site and then split the bond with highly acidic sites. If the polymer instead has some degree of unsaturation, it may be possible to use acid sites or metathesis catalysts alone to split the C=C bonds. Catalytic fractionation, where catalysts sequentially deconstruct varying bonds in a mixture in order of increasing strength [50], may also provide a useful framework for depolymerization. Catalyst recovery will also be a major consideration, especially for reactions like metathesis in which the materials are sensitive to air or moisture, and for reactions requiring physical mixtures of catalysts. Finally, deciding between applying either homogeneous or heterogeneous catalysts will necessitate an evaluation of the tradeoffs between the higher activity of homogeneous catalysts at low temperatures and the ease of separation of heterogeneous catalysts.

In this review, we have focused our discussion on polyolefins, leaving out polymers with heteroatoms and heteroatom bonds. However, if a process is intended to utilize a mixed plastic waste feedstock, it is crucial to account for the presence of non-uniformities in composition. Polymeric C-O bonds, for instance, are generally easier to break than C-C bonds, so under the harsher conditions required for C-C bond cleavage, the monomers from plastics like polyesters may not be preserved. In these cases, it may be important to consider advances in the preservation of C-O bonds during simultaneous breakage of C-C bonds. One such relevant study, provided by Jing et al., shows C-O bond preservation in the depolymerization of aromatics and lignin over Ru/Nb₂O₅ using site-selective methanol poisoning [118]. There are also additional considerations for chloride-containing polymers like polyvinyl chloride (PVC). PVC-containing feedstocks may require additional processing steps such as hydrodechlorination and dehydrochlorination – in these steps, an external hydrogen source may or may not be required depending on the importance of limiting catalyst deactivation [119].

As investigations are made to further plastics upcycling catalysis, it will be crucial to evaluate the economics of processing a given set of plastics and the marketability of the products. This will involve thorough technoeconomic and lifecycle analyses, which may necessitate similar analyses of adjacent and alternative systems [50]. Certain depolymerization technologies will inevitably be limited by their suitability in different economic and environmental situations. A hydrogen-dependent plastics upcycling process may be appropriate in a location with easy access to molecular hydrogen, but less so in a location with minimal access to hydrogen. It is therefore important to consider three things when designing a depolymerization process: the regional variability in access to given resources, the applicability of tandem technologies, and the market feasibility of both purchasing reagents and marketing products.

Finally, tangential considerations may assist in developing and applying plastics upcycling technology. Notably, there have been several advances in computational research focused on the kinetics of plastics or waste biomass upcycling as well as materials discovery [98, 120,121]. There is potential in applying these new computational methods as part of general evaluations of process feasibility. The optimization of each given process, especially when they depend on co-feeds or tandem processes, is also critical. In addition to these considerations, it will be eventually necessary to understand and transform the policy landscape to incentivize the emerging plastics upcycling industry. The development of catalytic processes such as metathesis, ring-opening polymerization, and other methods of addition and condensation have enabled the production of plastics we use in daily life. Now, the catalysis and chemical engineering community is tasked with employing these same methods to enable mild depolymerization and upcycling of waste polyolefins. Here, we have highlighted some promising means of enabling this depolymerization without the need to supply molecular H₂, a hopeful step towards an economical solution to the plastic waste

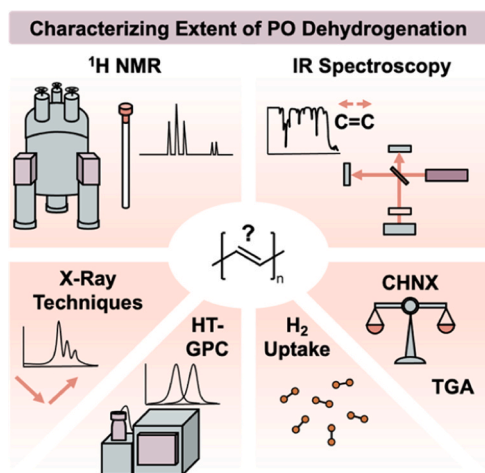


Fig. 6. Methods to characterize polyolefins after dehydrogenation/depolymerization reactions, which include ¹H NMR, infrared spectroscopy, high-temperature gel permeation chromatography (HT-GPC), thermogravimetric analysis (TGA), elemental analysis (EA or CHNX), measurement of hydrogen uptake from reduction of polymer, and x-ray scattering techniques.

crisis.

CRediT authorship contribution statement

Julia Hancock: Writing – Original Draft, Writing – Review & Editing, Julie Rorrer: Writing – Original Draft, Writing – Review & Editing, Conceptualization, Supervision.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

No data was used for the research described in the article.

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